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Partitioning of the source of leaf calcium of American beech and sugar maple using leaf Ca/Sr ratios: a predominantly surficial but variable depth of Ca uptake

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Short title: Calcium uptake depth of beech and maple

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Abstract

Background and Aims: Reduced availability of calcium (Ca) has been linked to maple forest decline. We therefore aimed at assessing the contribution of the different soil horizons to leaf Ca of competing beech (*Fagus grandifolia* Ehrh.) and sugar maple (*Acer saccharum* Marsh.) to better understand the dynamics of Ca uptake.

Methods: Leaf Ca was partitioned using the Ca/Sr ratio approach in two mature forests of southern Quebec. A mass balance was also used at one site to validate the results obtained with the Ca/Sr approach.

Results: The L and F horizons contributed most of the leaf Ca of beech and maple with likely small contributions from the upper B and/or H/Ahe horizons. Leaf Ca/Sr ratios of beech were however more variable than those of maple. Using a mass balance, the organic horizons and upper mineral soil horizons were found to provide ca. 80 and 20% of tree Ca uptake, respectively.

Conclusion: Beech and maple Ca uptake depth apportionment is on average similar but beech is likely more plastic in sourcing soil Ca. The low contribution of the mineral soil to leaf Ca at our sites can be linked to less favorable conditions for Ca uptake likely associated with low Ca/Al ratios.

Keywords: aluminum, beech, calcium uptake, mass balance, strontium, sugar maple

Introduction

Many forests of southern Quebec and eastern Ontario, as well as parts of eastern United States are considered marginally sufficient in Ca for good growth and health of sugar maple (Bailey et al. 2004; Duchesne et al. 2002; McLaughlin 1998). The reduced vigour of sugar maple (*Acer saccharum* Marsh.) in part of its range has been concomitant with a decrease in base cation availability on many sites (Bailey et al. 2004; Fenn et al. 2006; Watmough et al. 2005). In two regional studies on the effect of atmospheric acid deposition on forest ecosystems, a majority of sites in the hardwood forest of eastern Canada and New England states were found to exceed their critical acid load (McNulty et al. 2007; Ouimet et al. 2006). This suggests that the supply of Ca, the most abundant of the base cations, is generally decreasing in most of the hardwood forest range.

Although surficial soil organic horizons have been shown to be the main source of Ca for annual uptake in different forest types (Bélanger et al. 2012; Blum et al. 2008; Dambrine et al. 1997; Holmden and Bélanger 2010; Poszwa et al. 2002), the ultimate source of Ca over the history of the forest likely remains the mineral soil. Conifers and to a lesser extent beech were found to derive most of their Ca from the Ca-rich apatite found in the lower B horizons at the Hubbard Brook experimental forest, New Hampshire (Blum et al. 2002). The importance of the mineral soil for maple Ca nutrition is supported by the fact that maple forests in northeastern USA undergoing decline were found to occur primarily on sites with low Ca availability in the B horizon (Bailey et al. 2004). The bulk chemistry and mineralogy of a soil is therefore key in determining its long-term ability to withstand acidic deposition and to supply base cations such as Ca (Bailey 2000). With the relative ability of the different soil horizons to supply Ca being site and species specific, the partitioning of Ca uptake by horizon could provide a mechanistic explanation for the increase in American beech (*Fagus grandifolia* Ehrh.) population observed in many maple dominated forests of southern Quebec (Doyon et al. 2003; Duchesne and Ouimet 2009; Gravel et al. 2011) and in northeastern USA (Hane 2003).

Most of the fine roots of beech and sugar maple are typically located in the uppermost organic soil horizons (Yanai et al. 2008). Roots of beech are, however, smaller in diameter, have a higher specific root length and are more sparsely branched compared to sugar maple (Comas and Eissenstat 2004). Beech also produces root suckers that allow trees to be interconnected. The two species differ in terms of their mycorrhizal symbionts with beech forming ectomycorrhizae

(ECM), and sugar maple roots forming endomycorrhizae. Ectomycorrhizae have been shown to be capable of mineral weathering and to access nutrients directly from the mineral surfaces (Blum et al. 2002; Näsholm et al. 2009; Read et al. 2004), more so than endomycorrhizae (Quirk et al. 2012). This adaptation could be linked to a more efficient Ca uptake (Comas and Eissenstat 2004) and could confer a competitive advantage to trees with ECM like beech on poor soils (Read et al. 2004).

Calcium/Sr ratios have been useful to track Ca in soil-plant systems (Blum et al. 2002; 2008). Strontium closely matches Ca behavior in plant-soil systems because of its similar charge and ionic radius (Capo et al. 1998). However, a preferential plant uptake and translocation of Ca over Sr is usually observed (Bailey et al. 1996; Drouet and Herbauts 2008; Poszwa et al. 2000). Thus, typical increases in Ca/Sr range from 1.0 to 1.9 in plant tissue compared to the soil available fraction (Åberg et al. 1989; Beauregard and Côté 2008; Blum et al. 2000, 2012). Wood Ca/Sr along the bole of European beech (*Fagus sylvatica* L.) (Drouet and Herbauts 2008) and red pine (*Picea rubens* Sarg.) (Momoshima and Bondietti 1990) did not vary significantly, which suggests that the preferential uptake is at the soil/root and/or xylem/leaf interfaces. Correction for the preferential uptake of Ca over Sr is therefore necessary to identify or quantify the sources of Ca (Drouet and Herbauts 2008; Poszwa et al. 2000).

In this study, we used the Ca/Sr ratio approach to: 1) assess the contribution of the different soil horizons to leaf Ca uptake of beech in two mature hardwood stands developed in distinct ecological regions of southern Quebec and 2) compare beech and sugar maple leaf Ca uptake sources at one site. We hypothesized that beech, an ECM species, would rely less on the organic horizons (LFH) as a source of leaf Ca than sugar maple. A mass balance was also computed for one of the sites to validate the conclusions of the Ca/Sr approach. The development of a vertical gradient of Ca/Sr ratio during soil formation and the potential role of Al in restricting the depth of Ca uptake are discussed.

Materials and methods

Study sites

The study was conducted at two sites located in different ecological regions of southern Quebec, i.e., the Hermine watershed (HW) and the Morgan Arboretum (MA). The Hermine watershed is located at the *Station de Biologie des Laurentides*, in the Laurentian mountain region, 80 km north of Montreal Quebec (45º 59’ N, 74º 01’ W). It is a 5.1 ha northern hardwood forest watershed drained by an intermittent first-order stream. The catchment is part of the sugar maple and yellow birch biogeoclimatic region. The dominant canopy species in the watershed is sugar maple with beech, yellow birch (*Betula alleghaniensis* Britton), large-toothed aspen (*Populus grandidentata* Michx.), white birch (*Betula papyrifera* Marsh.), and balsam fir (*Abies balsamea* L.) as companion species, while striped maple (*Acer pennsylvanica* L.) and hobblebush (*Viburnum lantanoides* Michx.) are common in the understory. The soils are less than 2 m to bedrock and are sandy orthic or gleyed humo-ferric and ferro-humic podzols (Soil Classification Working Group 1998). The mineralogy of the bulk soils is relatively homogenous across the watershed and suggests a relatively high proportion of Ca-rich minerals (15% plagioclase feldspars, 4% and hornblende) but a small proportion of Ca-rich and easily weathered mineral (0.1% apatite) (Bélanger et al. 2012).

The Morgan Arboretum is located at the western tip of the island of Montreal (45º 25’N, 73º 57’ W). It is a 245 ha forested reserve on the McGill University Macdonald Campus and is part of the sugar maple and hickory biogeoclimatic region. The forest is dominated by sugar maple with many other hardwoods as companion species such as shagbark hickory (*Carya ovata* (Mill.) K. Koch), bitternut hickory (*Carya cordiformis* (Wangenh.) K. Koch), basswood (*Tilia americana* L.), white ash (*Fraxinus americana* L.), black cherry (*Prunus serotina* Ehrh.), and oaks (*Quercus* spp). Stands of beech can be found on wet and dry sandy soils generally in mixture with red maple (*Acer rubrum* L.). Sampling was done in a mature beech stand that had developed on a deep sandy ridge. The parent material is a stone-free, medium to fine sand of alluvial origin deposited over clay to a depth of 2-10 m. The soil is excessively drained and of very low fertility. It is underlain by the Beekmantown formation that is relatively high in dolomite (Lajoie and Baril 1954). Because of the thickness of the soil, the dolomite is beyond the reach of tree roots and has no detectable influence on soil chemistry. Soils were poorly developed ferro-humic podzol (Soil Classification Working Group 1998). Other characteristics are given in Table 1 for both sites.

Discrimination between Ca and Sr

Sampling

The assessment of discrimination between Ca and Sr of beech was done by sampling seedlings on a variety of soils that provided a wide range of soil Ca/Sr ratios. The small root system of seedlings allow for a limited soil volume to be explored that makes for a more accurate characterization of the Ca/Sr ratio of the pedogenic source of Ca. A similar approach was used successfully with sugar maple in a previous study (Beauregard and Côté 2008). Seedlings were sampled from 40 locations in natural forest stands located in HW and MA. Sampling consisted in pulling gently on the seedling to harvest most of the root system. It was first shaken gently to remove the soil that was weakly attached to the root system and then shaken more vigorously to remove the soil that was strongly attached. This second fraction is considered to be the extended rhizosphere, i.e. the soil used by the seedling through the root zone, and is therefore the fraction retained for the analysis. Sampled seedlings were less than 30 cm in height and were from one to six years old. All the seedling leaves were harvested and stored in paper bags in the field and on return to the laboratory, were dried at 65^{o}C for 48 h, and then ground. Soils were air-dried in the laboratory, ground gently with a rolling pin to break up coarse aggregates, and sieved to 2 mm.

Chemical analysis

Leaves were digested in concentrated HNO_3. The samples (0.1 g) were put in an open test tube (Pyrex 9860 rated for 500^{o}C) with 2 ml of 70% trace metal grade HNO_3 and left to react for 15 hours at room temperature. The tubes were covered with Parafilm™ to minimize contamination. The temperature was then increased gradually to 120°C and plant tissues were digested at this temperature for five hours. Samples were cooled and diluted with ultra pure water to a volume of 10 ml. Diluted samples were stored at 2ºC. The digestions were carried out in duplicate. Blanks, quality control and standards were run in each batch (20 samples). National Institute of Standards and Technology (NIST) reference sample 1547 (peach leaves) was used as a quality control. Leaf digests were analyzed for Ca and Sr by ICP-AES (Perkin-Elmer OPTIMA 43000V). Calcium and Sr values were all within the certified ranges for the standard (±1.3 % and 7.5 %, respectively) and blanks were all below the detection limit for both elements.

For the determination of Ca/Sr ratios in soils, samples were extracted using trace metal grade NH_4Cl (1.0 M) as described by Hendershot et al. (2007). Samples (soil:solution ratio of 1:10) were shaken for one hour, centrifuged at 5000 rpm for 10 minutes, and filtered through a 0.45 μm GE Magna nylon membrane. Extractions were carried out in duplicate, and stored at 2°C. Soil extracts were analyzed for Ca, Al and Sr by ICP-AES as indicated above for leaf analysis. Duplicate error was on average less than 3% for all combinations of elements and soil horizons. A soil sample from HW (BC horizon) was used as quality control for soil samples. Lab-ware for both leaf and soil analyses was washed in 15% HCl and then in 15% HNO_3 before use.

Relationship between leaf and soil Ca/Sr ratios of seedlings

As for sugar maple in Beauregard and Côté (2008), a linear regression was used to describe the relationship between leaf and soil Ca/Sr ratios of beech seedlings (Figure 1). The use of this approach was deemed necessary to facilitate comparisons of levels of preferential uptake and depth of Ca uptake between the two species. An analysis of residuals was performed to assess the accuracy of predictions across the range of soil Ca/Sr measured. The model used to predict soil Ca/Sr ratios was:

$$soil\ Ca/Sr = -16.3 + (0.48 \times leaf\ Ca/Sr) \qquad \text{[equation 1]}$$

with $R^2 = 0.52$, SEE = 68 and $p < 0.0001$ (Figure 1).

Application of the equation for values of 500 and 1000 mol mol^{-1}, a range that encompasses the range of leaf Ca/Sr ratios measured in the study, corresponds to discrimination factors (DF= ratio of the Ca/Sr ratio of the leaves and the Ca/Sr ratio of the NH_4 soil extract) of 2.24 and 2.16, values that fall within the range of DF (1.9 ± 1.2) determined by Dasch et al. (2006) and slightly above the range (1.78 ± 0.17) reported by Blum et al. (2012) for beech growing in northeastern USA. Application of the equation determined by Beauregard and Côté (2008) for sugar maple and for the same range of leaf Ca/Sr ratios as above would yield DF of 1.31 and 1.49, respectively. This is a lower range of DF than for beech, a result that is consistent with the observations of Dasch et al. (2006) and Blum et al. (2012). Our DF are, however, slightly higher than those reported in these two studies (1.14 ± 0.12 and 1.16 ± 0.13, respectively). The small differences in DF can be attributed to different methodological approaches e.g. leaves vs litter, summer vs fall sampling, digestion methods, and should have little effects on the outcome of their application to assess the contribution of different soil horizons to leaf Ca.

Tree height and leaf Ca/Sr ratios

A premise for the use of discrimination factors determined from seedlings for mature trees is that leaf Ca/Sr ratios are independent of the height of sampling. To test for this requirement, six beech trees were sampled at MA. All trees were growing on soils of the same series to reduce variation in leaf Ca/Sr among trees. Leaves of mature dominant trees were sampled in mid

August with a telescopic pole pruner. More than 30 leaves were taken at three different heights: 3, 6, and 13 m. Leaves were stored in paper bags in the field, and on return to the laboratory, dried at 65°C for two days to constant weight, and then ground and stored at room temperature. Leaves were digested and analyzed as described in the seedling study.

Partitioning of the source of leaf Ca

Soil sampling and analyses

Trees sampled at both sites were located within a small area (ca. 25 m radius) to reduce natural spatial variation in soil chemical properties. Two soil pits were dug at each site among the sampled trees. L, F and H horizons were sampled separately. The Ae/Ahe horizon was sampled in whole, whereas the rest of the soil profile was sampled in 10 cm increments down to at least 70 cm (B_{10}, B_{20} …B_{70}). An average of 0.5 L of soil was collected from each horizon. Soil samples were air dried, the aggregates broken, and then passed through a 2 mm mesh. Soils were extracted with trace metal grade NH_4Cl and analyzed for Ca, Sr and Al as described in the seedling study. Soil pH was measured in water using a ratio of soil:water of 1:10 and 1:2 for the organic and mineral soil horizons, respectively. Soil organic matter (loss on ignition) was determined by dry combustion (360°C for 4 h).

Leaf sampling and analyses

Leaves were sampled in August of 2009. Beech trees were mature dominant to co-dominant individuals at MA with diameters at breast height (DBH: 1.3 m aboveground) greater than 50 cm. At HW, most beech trees sampled were vigorous recruits with DBH between 10 and 20 cm with a few mature trees with DBH greater than 50 cm. Sugar maple trees were also sampled at HW with most trees being dominant to co-dominant with DBH greater than 40 cm. Sampling was done with a telescopic pole pruner. Leaves were sampled at mid-crown by harvesting branches exposed to direct sunlight. The composite sample was made of at least 30 leaves. They were stored in paper bags in the field and on return to the laboratory, oven dried at 65°C for at least two days until the weight was stable, and then ground and stored at room temperature. Leaves were digested and analyzed as described in the seedling study.

Determination of the main sources of leaf Ca

The model developed to describe the relationship between leaf and soil Ca/Sr ratios (equation 1) was used to calculate the soil Ca/Sr ratio that corresponds to the leaf Ca/Sr ratio of each tree, corrected for the discrimination between Ca and Sr, hereafter referred to as "corrected leaf Ca/Sr ratio". Although the corrected leaf Ca/Sr ratio can be attributed to a single soil horizon, it most probably represents the weighted average of the contribution of many soil horizons with different soil Ca/Sr ratios. Mixing equations were considered to partition tree Ca uptake among soil horizons, but differences in Ca/Sr ratios of the different horizons were too small to yield meaningful results. We therefore relied on a graphical/semi-quantitative approach to assess the contribution of each soil horizons.

To assess the validity of the estimated partitioning of the sources of Ca, a Ca mass balance was computed for HW. Nutrient monitoring at HW over a 10-year period allowed for the calculation of reliable estimates of the different pools and fluxes of Ca (Courchesne et al. 2005; Bélanger et al. 2002). For the purpose of the mass balance, the contribution of the different soil horizons to leaf Ca determined with the Ca/Sr approach was assumed to be the same as for the whole tree (leaves+bole+branches+roots). Details of the calculation for the determination of the different pools and transfers of Ca at HW are provided in the footnotes of Table 2.

Statistical analyses

A repeated measures ANOVA was used to test for the effect of height on leaf Ca/Sr ratios. Results are presented as the mean of percent variation in Ca/Sr within individual trees. STATISTICA 6 (Statsoft, 2004) was used for all statistics.

Results

The effect of height on leaf Ca/Sr ratio

No significant effect of height on leaf Ca/Sr ratio was detected (F = 1.55, p=0.27). Large variation in leaf Ca/Sr ratios were observed between trees (results not shown) but leaf Ca/Sr ratios for the 3, 6 and 13 m heights within individual trees did not vary significantly (Figure 2) with variation within a tree averaging less than ±5%. The preferential uptake of Ca over Sr is therefore likely limited to the bole/canopy interface and independent of the length of the bole as suggested by Drouet and Herbauts (2008). With a discrimination factor of 1.78 ± 0.17 for beech as measured by Blum et al. (2012), an overestimation or underestimation of a few percentage points would be of no consequence for the partitioning of leaf Ca/Sr. Therefore, the use of seedlings to determine the discrimination factor between Ca and Sr for leaves of mature beech was deemed justified.

Soil chemistry

Extractable Ca and Sr generally decreased with soil depth at both sites but the gradient was steeper at MA. Extractable Al was low in L and F horizons, but increased sharply in the H/Ahe horizons before decreasing with depth (Figures 3 and 4). Differences in these patterns were small between the sites. Soil pH was lowest in the Ahe horizon at both sites but otherwise generally increase with depth (Figures 3 and 4). Calcium/Al ratios of the L and F horizons were two orders of magnitude higher than those in the mineral horizons at HW and more than one order of magnitude higher at MA (Figures 3 and 4). Calcium/Al ratios of the mineral horizons showed small variation with depth at HW, whereas it reached a minimum at 30 cm before increasing in deeper soil at MA. At both sites, Ca/Al ratios were below 1 in the mineral horizons with lower values generally observed at MA (< 0.1). A steep vertical gradient of soil organic matter (SOM) was observed at both sites (Figures 3 and 4). Except for the F horizon, SOM was higher at HW at all depths with SOM remaining above 1% throughout the whole soil profile whereas SOM was less than 1% below the 30 cm depth at MA. A secondary peak in SOM was observed in the B_{10} at MA.

Soil Ca/Sr ratios generally decreased with depth but a bimodal trend with depth was observed with secondary peaks in the B_{10} and B_{10-30} at MA and HW, respectively. Soil Ca/Sr ratios showed a steep decreasing gradient along the L-F-H-Ahe horizons (Figure 5). The lowest Ca/Sr ratios were observed in the deepest soil horizons sampled.

Partitioning of the source of leaf Ca

Leaf Ca/Sr ratios of beech at HW averaged 770 ± 42 mol mol^{-1} with a range of 540 to 1114, whereas a mean leaf Ca/Sr ratio of 535 ± 55 mol mol^{-1} and a range of 450 to 660 were observed for MA. Corrected leaf Ca/Sr ratios are shown in Figure 5 together with the measured soil Ca/Sr ratios. At MA, the corrected leaf Ca/Sr ratio of beech (mean ± SE) intercepts only the measured Ca/Sr ratios of the L and F horizons. At HW the corrected leaf Ca/Sr ratio intercepts the measured soil Ca/Sr ratios of the L, F, B_{20} and B_{30} horizons. When considering the full variation in corrected leaf Ca/Sr ratios of beech observed, only one additional horizon (i.e. B_{10}) is intercepted at MA, whereas the B_{10} and B_{40} are also intercepted at HW.

Using the equation published in Beauregard and Côté (2008) describing the relationship between leaf and soil Ca/Sr ratios of sugar maple at HW, its corrected leaf Ca/Sr ratio (mean ± SE) intercepts the F, B_{20} and B_{30} horizons, and the L horizon is also included when the full variation in Ca/Sr ratios is considered (Figure 5).

The results of the mass balance produced for HW is shown in Table 2. In order to match the outputs measured in the zero-tension lysimeters located under the organic and mineral horizons (50 cm depth), an overall uptake of approximately 80% from the organic horizons (LFH) and 20% from the mineral horizons (Ahe + B_{10}-B_{50}) is required. The corresponding outputs below the organic and mineral horizons were estimated at 235 and 110 mol Ca ha^{-1} yr^{-1}, respectively (Table 2) compared to measured values of 230 and 85 mol Ca ha^{-1} yr^{-1}, respectively.

Discussion

Soil chemistry

Calcium availability was higher at HW, the likely result of a combination of factors. Apart from the different mineralogy that affects the rate of weathering and mineral composition of the soil solution, the finer soil texture and higher SOM of the mineral horizons at HW, through their effects on the soil CEC and water retention, likely contributed to the higher Ca availability and lower gradient with depth at that site. Although soil pH tended to increase with depth, a minimum was observed in the Ahe horizon. Aluminum showed a reverse pattern with maximum concentrations observed in the H-Ahe horizons. Together, both patterns with depth are typical of podzolic soils and indicate that the Ahe horizon was the most acidic at both sites (Courchesne and Hendershot 1997). The fact that the H horizon was as high in Al as the Ahe was however, unexpected, and is indicative of a higher level of acidity in that horizon relative to all others except for the Ahe.

The Ca/Al ratios were one or two order of magnitude higher in the L and F horizons than the mineral horizons. This steep gradient was the result of high Ca and low Al in the L and F horizons. Calcium/Al ratios below 1.0 in soil solution are generally considered toxic to roots or detrimental to Ca uptake (Cronan and Grigal 1995). Molar ratios of Ca/Al in NH_4Cl extracts at the HW varied between 2 and 3 mol mol^{-1} below the organic horizon and averaged 0.3 mol mol^{-1} at 50 cm in the mineral soil. Ca/Al molar ratios were monitored during one year at the HW and they averaged 3.2 ± 1.3 and 3.3 ± 1.2 mol mol^{-1} below the organic horizon and at a 50-cm depth in the mineral horizon, respectively (unpublished data). Comparisons of Ca/Al ratios of soil solution and NH_4Cl extracts suggest that no correction is needed for the organic horizon to assess the soil solution Ca/Al ratio but that Ca/Al ratios of NH_4Cl extracts have to be increased by a factor of 10 for the mineral horizon. Based on the critical ratio of 1.0 determined by Cronan and Grigal (1995), the H and the top 40 cm of mineral soil at MA can be considered less than optimal for Ca uptake.

Partitioning of the source of leaf Ca

At both sites, all beech trees had leaf Ca/Sr ratios (without correction for discrimination) that were higher than the highest soil Ca/Sr ratios observed for the whole soil profile (i.e. L and or F horizons). This is consistent with the strong discrimination observed in the seedling studies and by others for beech (Blum et al. 2012; Dasch et al. 2006). The corrected leaf Ca/Sr ratio (mean ± SD) of beech (based on the discrimination between Ca and Sr) corresponded best to the Ca/Sr ratio of the L and F horizons at both sites. Most of the leaf Ca of beech could therefore be accounted for by uptake from the L, F or a combination of L and F horizons. In another study, Blum et al. (2012) found that most of the leaf Ca of beech and other hardwoods could be accounted for by uptake from the Oie (L and F) horizon or a combination of Oie and Oa (H) horizons. The F horizon was therefore considered a likely major source of leaf Ca in both studies. In our study, the H horizon was an unlikely significant source of Ca based on its low Ca/Sr ratio. As for the contribution of the L horizon, although its Ca/Sr ratio corresponds to the corrected leaf Ca/Sr ratio, it also is an unlikely large source of leaf Ca because of the low mobility of Ca in leaf tissues associated with its structural role in leaves. We therefore conclude that the F horizon is likely the most important source of leaf Ca for beech at our sites. Bélanger et al. (2012) reached the same conclusion for HW using a combination of $^{87}Sr/^{86}Sr$, Ca/Sr and Ba/Sr ratios of the different soil fractions.

Although the contributions from the soil horizons other than the F are likely much smaller, they may be important to provide a sustainable supply of Ca over the longer term. The B_{20}-B_{30} at HW also intercepts the corrected leaf Ca/Sr ratio (mean ± SE), but to a lesser degree than the L and F horizons. This suggests that some of the upper B horizons are also a likely significant source of leaf Ca for beech at HW. Moreover, when considering the lowest and highest corrected leaf Ca/Sr ratios, the Ca/Sr ratios of the B_{10} and B_{40} horizons at HW are also intercepting the corrected leaf Ca/Sr ratios of beech. If one were to use these extreme values with mixing equations, many trees with high Ca/Sr ratios would be found to rely almost exclusively on L and F horizons whereas some trees with low Ca/Sr ratios would be found to rely substantially on H and/or upper B horizons for their Ca supply. These results suggest that beech can meet its Ca requirements through uptake from different soil pools located at different depths.

The partitioning of the source of leaf Ca for sugar maple at HW does not yield clear results. Although the corrected leaf Ca/Sr ratios intercept the L, F and B_{20}-B_{30} horizons, numerous combinations of soil horizons could explain the measured leaf Ca/Sr ratios of sugar maple. The most likely scenario based on the conclusions of other studies (Bélanger et al. 2012; Blum et al. 2008, 2012) would be that the L and F horizons are the primary source of Ca with minor contributions from the H, Ahe and upper B horizons. Using the lowest and highest corrected leaf Ca/Sr ratios observed provides for a smaller range of leaf Ca/Sr ratio for maple than for beech and, therefore, less extreme scenarios of uptake depth for maple. On average, beech seems to rely more on the organic horizons as its primary source of leaf Ca than sugar maple while demonstrating more plasticity in its sourcing of soil Ca at HW. The dominance of beech at MA on a nutrient poor sandy soil also suggests that it is better adapted than sugar maple to rely almost exclusively on the organic horizons for its source of leaf Ca on poor sites with very limited sources of easily weathered Ca-rich minerals (e.g. apatite) in deeper soil horizons.

The small reliance of most beech on the mineral horizons for leaf Ca at HW is somewhat surprising considering that many roots can be found in the upper 30 cm of mineral soil. Calcium availability in the mineral horizons at HW is one order of magnitude higher than at MA, and although a slightly higher proportion of leaf Ca is likely provided by the upper B horizons at that site (Figure 5), most beech still seems to rely primarily on the organic horizons for their Ca supply at HW. Soil pH is higher at both sites in the mineral soil (ca. pH=5) than in the organic horizons, the main source of Ca for both species. These observations suggest that neither Ca availability nor soil pH is a limiting factor for Ca uptake in the mineral soil at both sites. The Ca/Al ratio of the B horizon soil solution estimated from soil extracts is, however, less than 1 at MA. A ratio of less than 1 for Ca/Al is often considered less than optimal for tree nutrition (Cronan and Grigal 1995; Lyon and Sharpe 1999). Oxides of Fe and Al that coat soil particles in podzolic B horizons can also isolate the fresh Ca-rich minerals from moisture and, hence, decrease the release of Ca in the soil solution from weathering reactions as well as its availability to tree roots (Courchesne et al. 1996; Gustafsson et al. 2000). Thus, the chemistry of the B horizons at MA compared to the L and F horizons is not likely to be as conducive to Ca uptake and could explain the smaller reliance of beech on mineral soil for Ca uptake at MA compared to HW. Nevertheless, the monitoring of nutrient cycling at HW has revealed that exchangeable Ca has decreased more in the mineral soil than in the organic horizons during the period of 1993 to 2002 (Courchesne et al. 2005). Hence, conditions for Ca uptake in the podzolic B horizons are likely worsening at HW and are likely to continue to acidify according to dynamic process-oriented models (Bélanger et al. 2002).

Given that low Ca availability of the mineral soil was associated with sugar maple decline and low nutrient status (Bailey et al. 2004), the contribution of the podzolic B horizons to Ca uptake, although small, is likely to be critical to tree nutrition and to the replenishment of the more surficial soil horizons. At Hubbard Brook, as much as 20% of the exchangeable Ca in the Oa horizon is derived from apatite located in the podzolic B horizons (Blum et al. 2002). Similarly, Dijkstra and Smits (2002) showed that only a small amount of Ca uptake from deep soil horizons (> 20 cm) was necessary to sustain Ca availability in the surface soil. Our results suggest a small but significant uptake of Ca from the upper B horizons, particularly at HW for both species. Such “pumping” of Ca derived from the slow weathering of the anorthosite (Ca-rich plagioclase and hornblende) at HW (Bélanger et al. 2012) may explain why the maple forest has not developed severe Ca deficiencies (Vizcayno-Soto and Côté 2004) and undergone significant forest decline at that site.

Mass balance

The Ca mass balance for HW reveals that outputs measured from lysimeters installed below the organic horizons and at 50 cm in the mineral horizon can be matched with contributions of 80 and 20% of Ca supply from the organic and mineral horizons, respectively. However, using a mass balance does not allow for a differentiation between the Ca uptake of different species. At HW where sugar maple dominates and beech is a companion species, results reflect the weighted contribution of both species. Given the small percentage of beech in the watershed, the 80:20 ratio should apply primarily to sugar maple. The greater reliance of most beech on organic soil horizons for Ca supply, based on its higher corrected leaf Ca/Sr ratios, suggest that it is relying on these horizons for more than 80% of its Ca supply. Beech trees were on average much smaller and younger than sugar maple in the watershed as many of them are gaining dominance following the decline of sugar maple in the 1980's. The larger size of sugar maples and likely deeper root systems may have contributed to lowering the leaf Ca/Sr ratios due to deeper Ca uptake. The lower leaf Ca/Sr of sugar maple could also be explained by a significant Ca uptake from the H and Ahe horizons. Although quite acidic (ca. pH = 4), their Ca/Al ratios were close to 1.0 or slightly above which is conducive to Ca uptake. Significant Ca uptake from these two horizons would decrease our estimates of the contributions of the upper B horizons to levels that are more in line with results from other studies with a predominant Ca uptake from the organic horizons (Blum et al. 2008, 2012; Bélanger et al. 2012).

Soil Ca/Sr ratios

Soil Ca/Sr ratios were generally higher in the organic horizons than in the mineral horizons. This is consistent with the observation of others (Dijkstra and Smits 2002; Poszwa et al. 2000) and can be explained in part by the cycling of Ca and Sr in the soil/plant system. The preferential translocation of Ca over Sr in leaves of many hardwoods is well documented (Blum et al. 2008, 2012; Bullen and Bailey 2005; Dasch et al. 2006; Poszwa et al. 2000). The enrichment of the leaves in Ca relative to Sr, and their subsequent deposition on the forest floor is likely the main mechanism for the steep gradient observed with depth at both sites. Given that beech discriminates more than sugar maple against Sr, one would expect a stronger gradient in soil Ca/Sr ratio with depth. Comparison of the soil profiles at HW and MA supports this hypothesis with the beech stand at MA showing a steeper gradient than the maple stand at HW (Figure 5).

The secondary maximum in Ca/Sr ratios observed in the B_{10} at MA and from B_{10} to B_{40} at HW cannot, however, be attributed to direct enrichment associated with the deposition of leaf litter. Both soils are podzols with Ae and Ahe horizons characterized by intense weathering and leaching. The low Ca/Sr ratio of deep soil horizons suggests that the weathering is not directly responsible for the secondary maximum in Ca/Sr ratio observed in the upper B horizons at both sites. Thus, the leaching and subsequent deposition of Ca and Sr from the Ae to the upper B horizons are more likely responsible for the secondary maximum. For this process to cause an increase in Ca/Sr ratio, a differential leaching of Ca over Sr in the Ae/Ahe and/or a selective retention in the upper B horizons would be required. Although Ca and Sr are often considered to behave similarly in the soil plant systems, the large differences in soil Ca/Sr ratios observed in different soil fractions (Beauregard and Côté 2008; Bélanger et al. 2012; Blum et al. 2002) suggest otherwise. Lefevre et al. (1996) showed that Ca and Sr are retained with the same strength by mineral soil particles whereas Baes and Bloom (1988) demonstrated that organic matter preferentially adsorbs Ca. The secondary peaks in Ca/Sr could therefore be partly due to enrichment in Ca over Sr in the carbon-rich upper podzolic B whereas the Ca/Sr ratio would decrease again deeper in the soil profile with decreasing SOM. The similarity between the soil profiles in Ca/Sr and SOM at MA supports this hypothesis but other factors are likely involved at HW where the secondary maximum in Ca/Sr ratio observed in the B_{20}-B_{30} was not matched by a similar increase in SOM.

Conclusion

On two sites contrasting in climatic conditions, soil physical and chemical characteristics and tree species composition, beech was found to rely primarily on the organic soil horizons for Ca nutrition. Depth of Ca uptake is, however, likely quite variable among individual beech trees, which may reflect the large spatial variation in Ca availability and/or its plasticity to tap Ca from different sources. At HW, most beech are likely relying more on surficial soil horizons than sugar maple but both species rely on a small contribution from the mineral soil to leaf Ca. The low concentration in Ca-rich and easily weathered minerals and less favorable conditions for Ca uptake linked to low Ca/Al ratios could explain this small contribution. Whether the capacity of beech to rely on organic soil horizons as its sole source of Ca on Ca poor soils can provide enough of a competitive advantage over the more Ca-demanding and Al-sensitive sugar maple to explain its increasing dominance at HW and in other hardwood forests of southern Quebec remain to be demonstrated.

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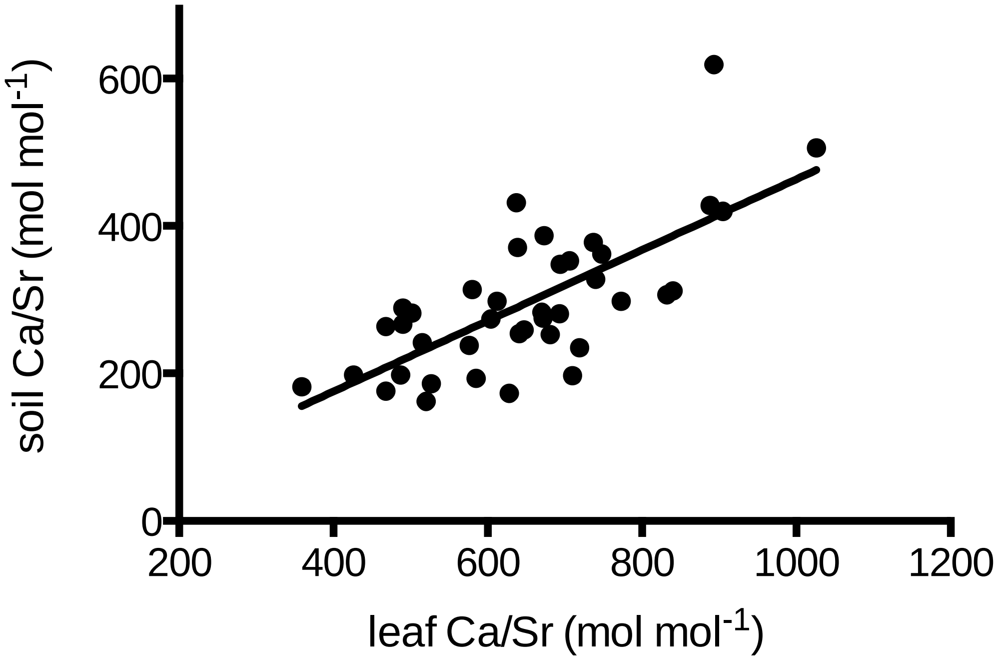

Fig. 1 Relationship between leaf Ca/Sr ratios of American beech seedlings and the Ca/Sr ratios of their extended rhizospheric soil

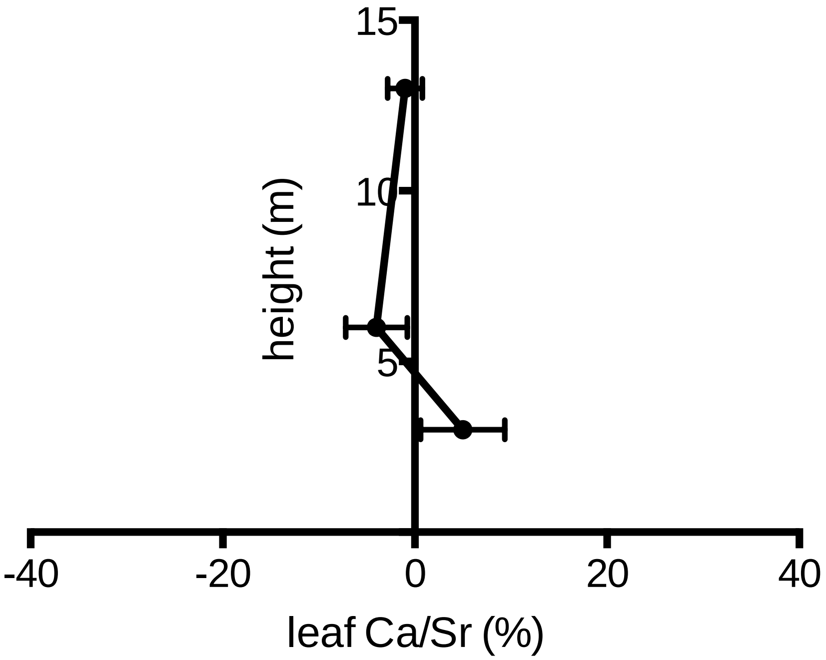

Fig. 2 Effect of height of sampling on the leaf Ca/Sr ratio of mature American beech (mean ± SE; N=6). Note: values are calculated as percent of the mean leaf Ca/Sr ratio of the three heights

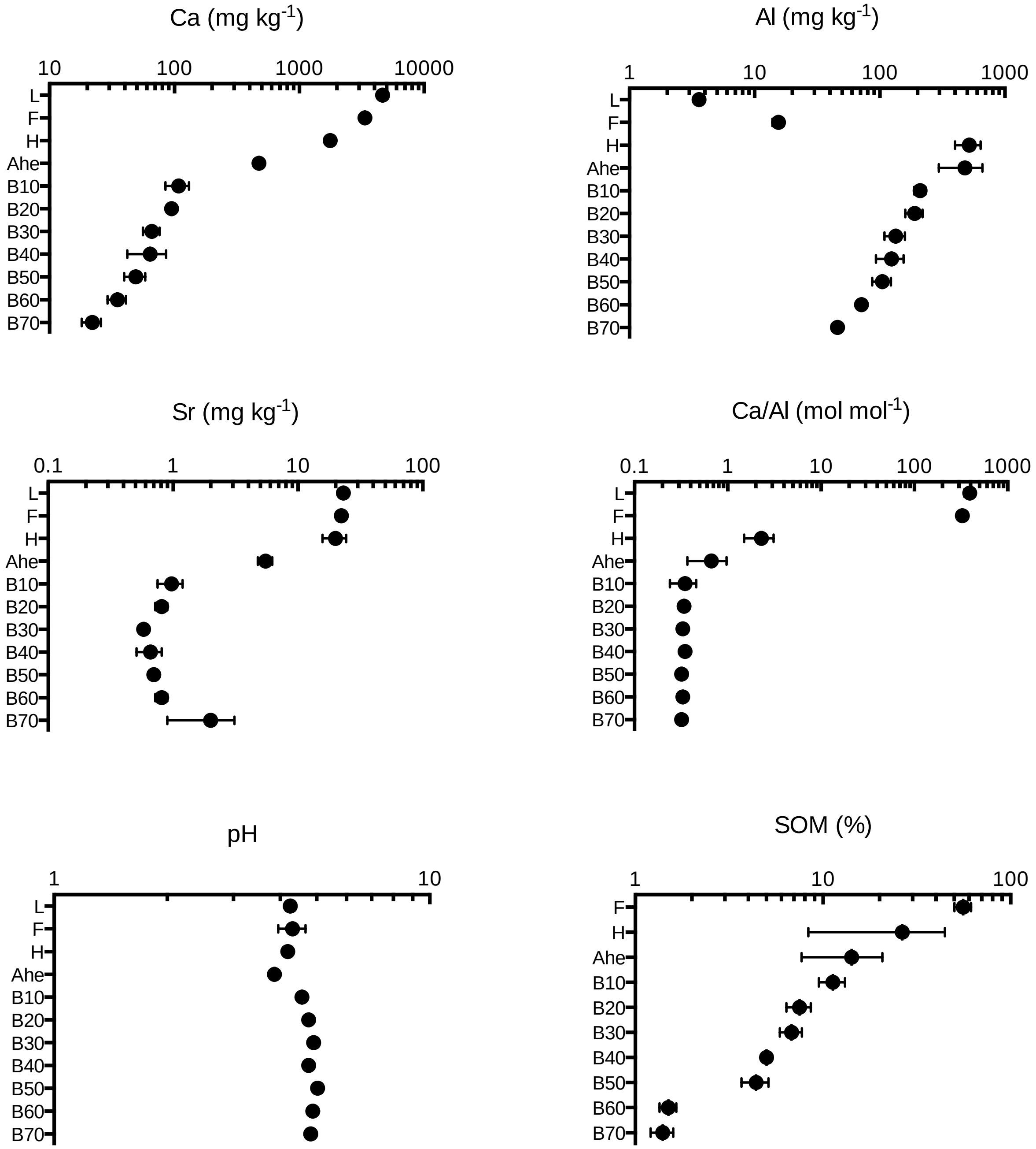

Fig. 3 Soil extractable Ca, Sr, and Al, Ca/Al ratios, soil pH and soil organic matter (SOM) (mean ± SD; N=2) by soil horizons and/or depth at the Hermine watershed

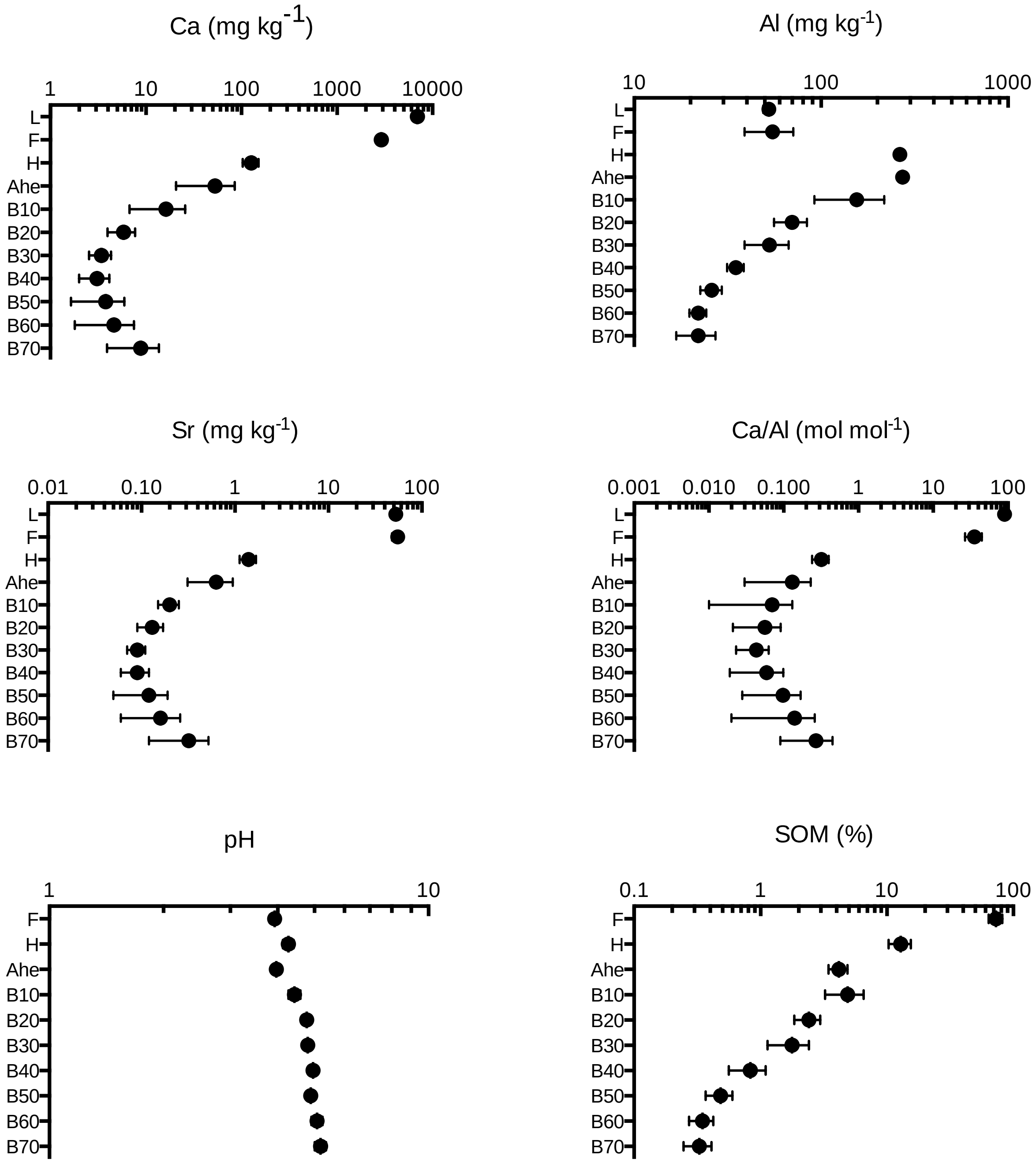

Fig. 4 Soil extractable Ca, Sr, and Al, Ca/Al ratios, soil pH and soil organic matter (SOM) (mean ± SD; N=2) by soil horizons and or depth at the Morgan Arboretum

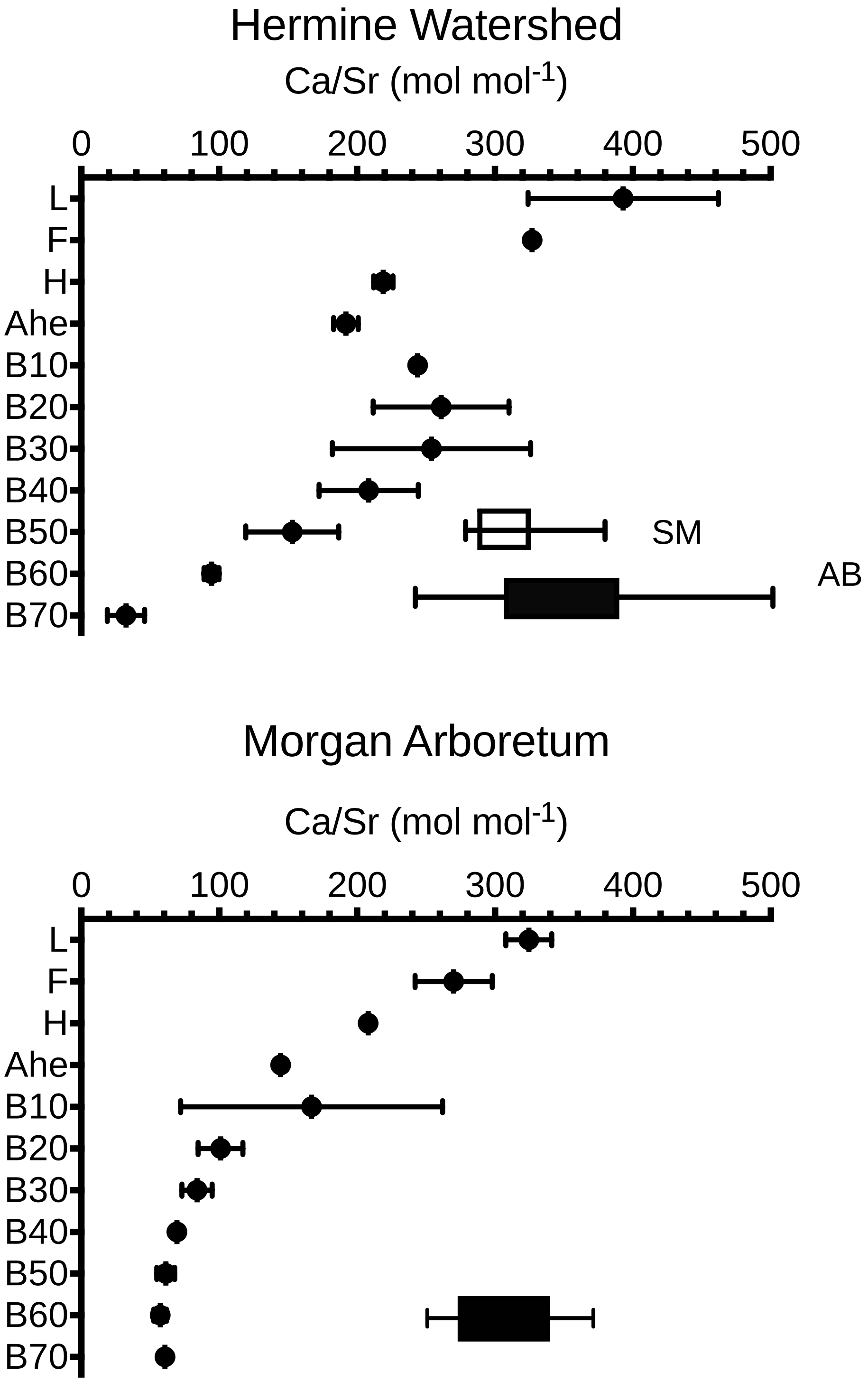

Fig. 5 Soil Ca/Sr ratios by soil horizon at the two study sites and range of corrected leaf Ca/Sr ratios of American beech (AB) and sugar maple (SM); box = mean ± SD, error bars = lowest and highest values observed

Table 1 Description of the study sites.

Characteristics	Hermine Watershed	Morgan Arboretum
Latitude	45º 59’ N	45º 25’N
Longitude	74º 01’ W	73º 57’ W
Altitude (m)	380	15
Overstory age (yr)	90	50-150
Origin	fire	cut
Basal area (m^2 ha^{-1})	29.1 ± 1.6	20-40
Canopy height (m)	20-25	25-35
Mean July air temperature (ºC)	20	20.9
Mean December air temperature (ºC)	-10	-6.6
Mean annual precipitation (mm)	1100 (30% as snow)	929 (20% as snow)
Soil depth (m)	1-2	>2
Parent material	till	fluvioglacial
Soil texture	sandy loam	sand
Soil type	podzol	podzol
Humus type	moder	mor
Drainage	moderate	very fast

Table 2 Calcium mass balance for the Hermine watershed; a 870:230 ratio of Ca uptake from the organic and upper 50 cm of the mineral horizons is used to match measured lysimeter outputs.

Tree Ca uptake	**mol ha^{-1} yr^{-1}**
leaves[a]	500
stemwood/bark[b]	170
roots[c]	34
fine roots[d]	385
throughflow[e]	18026
TOTAL	126915

Soil input/output	**mol ha^{-1} yr^{-1}**
Aboveground input	
throughfall	275192
leaf litter[f]	50050
wood litter[g]	15570
TOTAL	93012
LFH	
small root litter[h]	308
root litter	12
tree uptake	-1015850 (870%)
output-lysimeter[i]	235382 (vs 230400 measured)
Ahe, Ae and B horizons down to 50 cm	
small root litter	77
root litter	2230
weathering[j]	312
tree uptake	-254365 (230%)
output-lysimeter	11147 (vs 85134 measured)

a. Leaf canopy Ca: from median of range of leaf litterfall dry weight (from Courchesne et al. (2001) and multiplied by leaf Ca concentration at HW (from Bélanger et al. (2002)
b. Net annual wood Ca uptake: Ca content of wood and bark /age of forest; based on forest inventory and allometric equations from Boucher and Côté (2002)
c. Root Ca: 20% of aboveground wood Ca as in Whittaker et al. (1979)
d. Annual fine root Ca immobilization: median of range of annual fine root production based on rhizotron sampling at HW over several years (Courchesne et al. 2001) and; an average concentration of 4 mg g^{-1} of Ca was
e. assumed to calculate annual fine root Ca immobilization
f. Throughflow: throughfall – wet deposition; wet Ca deposition at HW from: average values reported in Bélanger et al. (2002) and Courchesne et al. (2001)) and adjusted for the length of growing season (snow free); throughfall Ca: fromas reported in Bélanger et al. (2002)
g. Leaf litter Ca: from Courchesne et al. (2001)leaf canopy Ca increased by 10% for litterfall as reported in Whittaker et al. (1979) and Duchesne et al. 2001
h. set at 90% of wood Ca uptake based on Wood litter: nul since net growth was nul in years of sampling and SOM buildup,
i. annual wood Ca litter is assumed to be the same as the net annual wood Ca uptake
j. dDistribution of root litter among soil horizon : 80% in organic horizons and 20% in mineral horizons for fine roots; 65% in organic horizons and 35% in mineral for large roots was (adapted from Badibanga et al. (1992)
k. Lysimeter: product of Ca concentration (Courchesne et al. 2001)s and water flux at HW; water flux set at assuming 70 % and 55% of incident precipitation (Courchesne et al. (2001)Pi under the organic horizon and at 50s cm and 55% at 50 cm in the B horizon, respectively (Courchesne et al. 2001);
l. values were adjusted for the length of growing season (snow free)
m. wWeathering at HW (: as measured by Courchesne et al. (2002); allocated in proportion of soil horizon depth considered (A_e, B_{50} and BC horizons)